

**ROLE OF VARIOUS PARAMETERS IN THE
SYNTHESIS OF INSOLUBLE XANTHATES
FOR HEAVY METALS REMOVAL FROM
WATERS**

A Thesis Submitted
in Partial Fulfillment of the Requirements
for the Degree of
Master of Technology

by
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to the
DEPARTMENT OF CIVIL ENGINEERING
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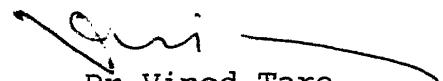
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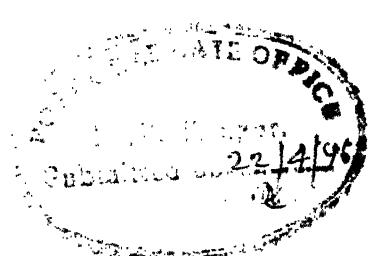
**To
My Parents**

CERTIFICATE

Certified that the work presented in this thesis entitled "*Role of Various Parameters in the Synthesis of Insoluble Xanthate for Heavy Metals Removal from Waters*" by *Ms Saswati Chakraborty* has been carried out under my supervision.


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- Saswati

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ABSTRACT

The present research attempts to identify and study the influence of various parameters involved in the synthesis of insoluble agrobased xanthates used for heavy metal removal from waters. Emphasis has been laid on alkalization and xanthation step. The three agrobased materials, namely wood, baggase and corn stalk, which are reported to have high potential for xanthation have been used. The relative degree of xanthation is determined through estimation of copper loading. Results indicate that (i) minimum alkali strength of 4 M is required for maximum xanthation, (ii) significance of stirring in alkalization step depends on the base material used, (iii) a contact time of 2-3 h is most appropriate during alkalization, (iv) the amount of base material that can be added to a known volume of alkaline solution is governed by the ability to get good working consistency, (v) only strong bases are effective in xanthation and mother liquor could be reused several times without sacrificing on degree of xanthation, (vi) stirring during xanthation step is important and a stirring time of 4 h is required which is irrespective of the base material chosen, and (vii) an optimum CS₂:BM ratio of 1.25 is to be maintained for maximum degree of xanthation.

Attempts made to develop a simple measure for getting an idea about degree of xanthation suggest that Iodine value can be used as an indirect estimate of degree of xanthation and metal binding capacity of IAXs.

KEY WORDS

Heavy metals, Agrobased xanthates, Insoluble xanthates, Xanthate synthesis, Sorption, Physicochemical processes, Wastewater treatment.

1. INTRODUCTION

Chemical contamination throughout the environment is typical of our advanced technological society. One of the special characteristics of an industrialised society is high consumption of metals because of their widespread use in various fields.

It is known for a long time that metal ions play either a positive or negative role on biological system. In the later half of this century, some metal ions, called "Heavy Metals", have drawn increasing human attention because of certain incidents, such as Minamata disaster, Itai-itai disease, lung cancer on Hokkaido island, etc.

A specific definition of heavy metals, which could be accepted universally, is not available. In some references, metals having density at least five times greater than water are referred as heavy metals. However, the word heavy metal is associated with connotations of toxicity and include metals such as arsenic, cadmium, chromium, copper, iron, lead, mercury, nickel, niobium, silver, tin, titanium, vanadium and zinc. Most of them are classified as priority pollutants by the United States Environmental Protection Agency (USEPA). As such limits have been placed on their concentrations in potable water, in sources of abstraction and in effluent discharges.

With the introduction of environmental regulations, various treatment technologies have been developed. Any treatment method must

enable:

- achievement of the set discharge limits,
- the recovery of precious metal ions, and
- be economically viable to the industry.

None of the various available treatment technologies can fulfil these three requirements simultaneously.

Out of the various innovative treatment technologies, xanthate process has focused attention as one of the most promising one. Xanthates, synthesized for metal removal from waters are starch and cellulose based polymer and are very specific in interaction with metal ions. It is well known that starch and cellulose consist of glucose units connected by α or β linkage and posses several hydroxyl groups. In the presence of excess alkali, the hydrogen is removed from starch and CS_2 combines to yield corresponding metal (from alkali) xanthate. Xanthates, soluble in water before reacting with metal ions have been termed as soluble xanthates (SX) while insoluble xanthates (IX) are the ones which can be easily separated by simple settling.

Soluble starch xanthate (SSX) is synthesized using soluble starch and makes a very fine colloidal suspension, which is difficult to destabilize. Metal removal efficiency critically depends on the dose of SSX. Insoluble starch xanthate (ISX) is synthesized from highly crosslinked starch, which is insoluble. The synthesis becomes complicated and expensive because of elaborate crosslinking operation. But no additional effort is required for the separation of metal bound ISX and metal removal is not adversely affected by over-dosing as in the case of metal-SSX system.

The expensive and elaborate crosslinking in ISX synthesis can be eliminated by using naturally available low cost agro-based materials. They are insoluble and contain large amount of cellulose and the xanthates synthesized from them are termed as insoluble agrobased xanthate (IAX). IAXs are reported to be highly efficient in removing heavy metals satisfying the required discharge limits at a relatively low dose. At present very limited information is available on the synthesis and application of agrobased xanthates for the removal and recovery of heavy metals from waters. The major thrust in the present research has been to improve the state-of-the-art on IAX process with emphasis on analysing the role of various parameters in synthesis of agrobased xanthates.

2. BACKGROUND INFORMATION AND LITERATURE REVIEW

Heavy Metals enter in the aquatic system from a variety of sources. The sources may be natural or anthropogenic. The major anthropogenic activities resulting in metal contamination causing serious environmental threats encompass domestic, mining and industrial sectors. It is quite clear that industrial discharges are mainly responsible for heavy metal pollution in the aquatic environment.

2.1 Heavy Metal Toxicity

Although some of the heavy metals like copper are essential at micro level, it is beyond doubt that most of them are potentially hazardous to the living system. Some are toxic at high concentrations, and a few are severe poisons even at very low concentrations. Heavy

metal ions cause toxicity by interfering with the metabolic reactions in the cell. If this reaction occurs in an important part of the cell, the cell will definitely die. Otherwise it may alter the cell structure and function, thus affecting the performance of the whole system. Again, some metals are suspected to be carcinogenic in nature, for example, nickel is supposed to produce cancer in respiratory tract while lead is suspected to cause kidney cancer.

2.2 Effluent Standards and Drinking Water Limits

Considering the harmful effects of heavy metals, limits have been placed on their concentration in potable water supplies and effluent discharges by different control agencies throughout the world. Some typical standards for heavy metals are given in Table 2.1. There is a wide variation between standards accepted by different agencies, which may be due to economical viability of control mechanisms.

2.3 Overview of Treatment Technologies

The introduction of the regulations for effluent standard necessitates the development of various treatment technologies. The treatment technologies, in general, can be of two types:

1. destructive technologies, and
2. recovery technologies.

Traditional chemical precipitation which include hydroxide, sulfide or carbonate precipitation and oxidation-reduction followed by

Table 2.1: Some Typical Industrial Effluent Discharge and Drinking Water Standards for Heavy Metals
(Chaudhari, 1993)

Metal	Industrial Discharge Limits, mg/l									Drinking Water	
	UPPCB			BIS ¹			WHO			WHO	
	A	B ²	C	A	B	C	A	B	C	Acceptable	Cause for Rejection ⁴
Arsenic	0.2	-	0.5	0.2	-	-	0.5	0.5	0.8	0.05	0.05
Cadmium	2.0	-	5.0	2.0	-	-	0.1	0.1	0.1	0.1	0.1
Chromium (VI)	0.1	-	1.0	0.1	2.0	-	-	-	-	0.5	0.5
Chromium (Total)	0.5	-	2.5	-	-	-	-	-	-	-	-
Copper	3.0	-	3.0	3.0	3.0	-	0.5	0.5	0.5	0.05	1.5
Lead	0.1	-	0.5	0.1	1.0	-	0.1	0.1	0.1	0.1	0.1
Mercury	0.01	-	0.01	0.1	-	-	0.001	0.001	0.001	0.001	0.001
Nickle	3.0	-	3.0	3.0	2.0	-	-	-	-	-	-
Zinc	5.2		10.0	5.0	15.0		5.15	5.15	5.15	5.0	15.0

A : into inland water

B : into public sewer

C : on land

UPPCB : U.P. Pollution Control Board

BIS : Bureau of Indian Standard

WHO : World Health Organisation

1. BIS 2490 (1974) Tolerance limits for industrial effluents discharged into inland surface waters (Part II)
2. Same as A and C depending upon the final recipient being either water course or land.
3. These are the limits up to which the water is generally acceptable to the consumers.
4. Tolerable in the absence of alternative and better source but above which the supply will have to be rejected.

precipitation are claimed to be economical (Patterson, 1975). But these are not able to meet the stringent effluent standards, specially in presence of complexing agents (Yost and Scarfi, 1979a,b; Karra et al., 1985). On the other hand, other advanced technologies, like, ion-exchange, reverse osmosis, electrodialysis, etc. are not economically acceptable. So with the available treatment technologies it is almost impossible to satisfy the economics and regulatory effluent standards simultaneously. This demands for the development of new technologies which are specific for heavy metal removal and are less expensive. Biosorption, starch xanthate process and various other innovative and emerging technologies can fulfil these demands but there are many questions yet to be answered by the advocates of these technologies.

2.4 Xanthate: Definition and Characteristics

Xanthates are polymers with specific functional group to bind metal ions. They are recognised as a class of sulfur compounds having starch and cellulose base. Strong alkali solutions acting on cellulose at low or room temperature produce alkali cellulose. This treatment of cellulose has been known for a long time as mercerization. When this alkali cellulose is treated with carbon-di-sulfide, interaction occurs with the formation of a sodium salt of the cellulose ester of dithiocarbonic acid, more familiarly known as cellulose xanthate.

In this reaction the intermediate product is alkali cellulose, which is a result of chemical combination between cellulose and sodium hydroxide and is susceptible to decomposition under the

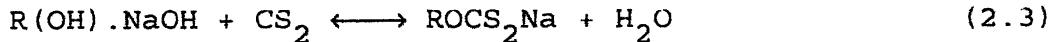
action of water. The two different views exist on the formation of this alkali cellulose (Ott *et al.*, 1954). First one is, like the simple alcohols, cellulose forms a true alcoholate with metal ions (M) substituting for hydrogen ion and this can be represented by:



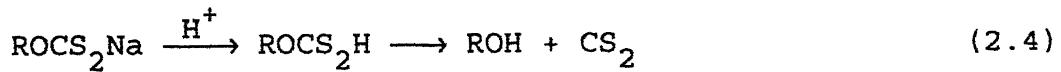
and the second one is that alkali acts as an addition complex to form alkali cellulose (Makolkin, 1943) which is represented by:



Although the literature indicates the differences in opinion on this point, the majority of investigators in this field seem to agree that, in the presence of water the addition complex is to be preferred over the alcoholate type of structure and hence alkali cellulose is a product of the addition of alkali to cellulose in the form of weak electrolyte and not in the form of an alcoholate. In this thesis, this reaction is referred as alkaliisation whereas, combination with carbon-di-sulfide to form cellulose xanthate is described as xanthation and is represented by:



Free xanthic acid can be obtained by acidifying cellulose xanthate. But it is quite unstable and decomposes back to alcohol and carbon-di-sulfide, which is irreversible reaction (Iwasaki and Cooke, 1958) :



2.5 Types of Xanthates and Their Historical Development

Depending on the solubility of xanthates in water before reacting with metal ions, they are classified in two types - soluble starch xanthate (SSX) and insoluble starch xanthate (ISX). A brief historical development of xanthate process is presented in Figure 2.1. At first, xanthate group has focused attention due to its high specificity towards metal ions. Then SSX was synthesized and was proved to be effective in metal removal. This was followed by improvement in the separation of metal-SSX complex by adding several polyelectrolytes. Further ISX was synthesized for metal removal from the aqueous system. Recent modifications of ISX include development of insoluble agrobased xanthate (IAX).

2.6 Soluble Starch Xanthate (SSX)

Xanthation of starch proceeds readily in strong alkaline condition. Starch consists of several OH groups and general formula is $-\left(C_6H_{10}O_5\right)_x$. It occurs in a wide variety of food products (corn, wheat, potatoes, rice, etc.). The structure of starch molecule is not known definitely. Starches are composed of two polysaccharide fractions - amylose and amylopectin and their ratio is different for different types of starch. Amylose molecule contains 100 to 1000 glucose units connected in a straight chain by $\alpha - 1, 6$ linkages. Amylose is soluble in water. Amylopectin molecule is much larger and contains nearly 500 to 5000 glucose units by $\alpha - 1, 6$ linkage to form branched chain. They are not as soluble in water as amylose. The hydroxyl group is the primary group which is involved in xanthation

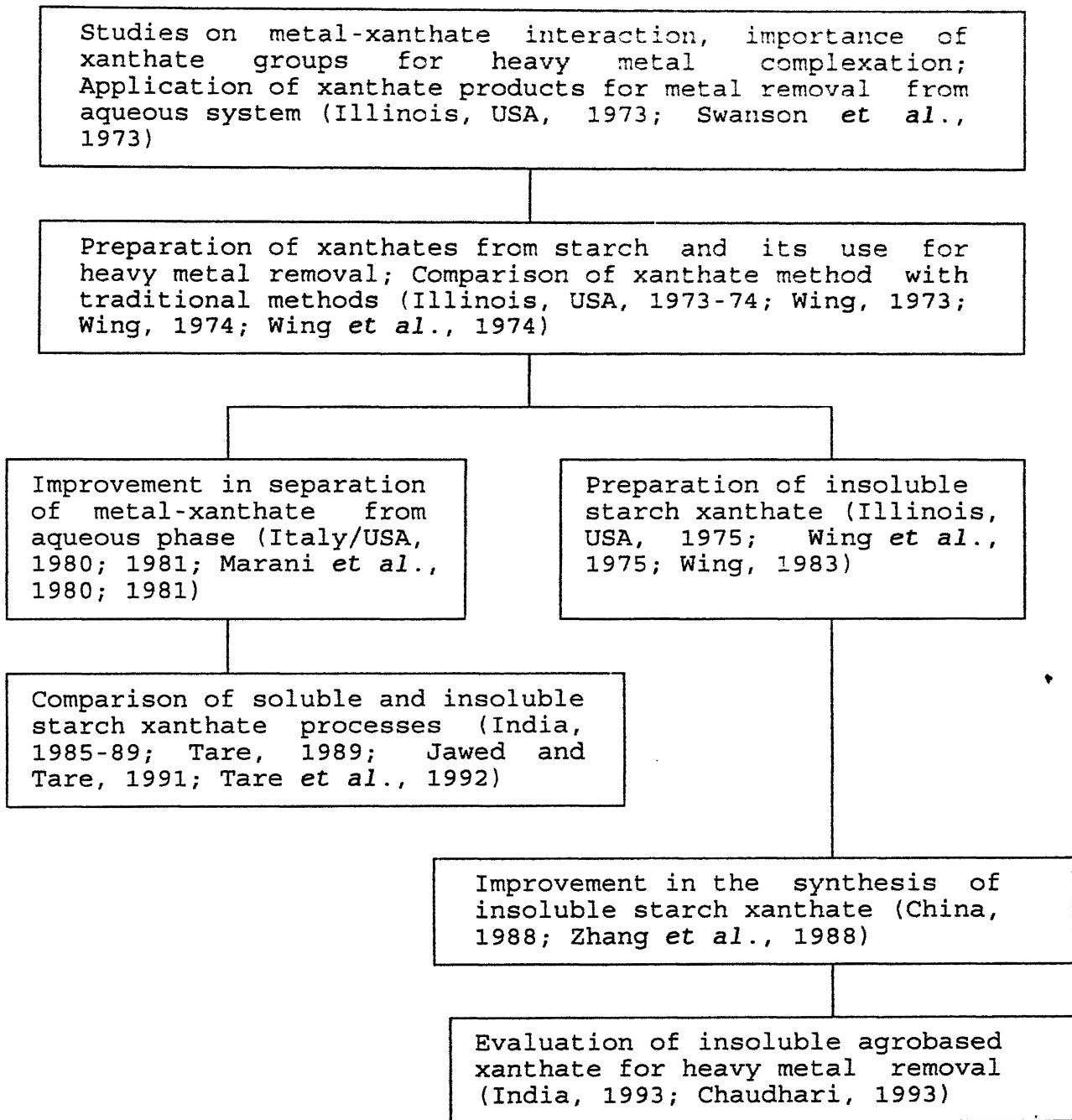


Fig. 2.1: Historical Development of Xanthate Process.

reaction (Sawyer and McCarty, 1994).

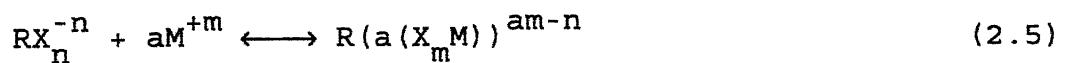
2.6.1 **Synthesis of SSX**

SSX is synthesized in two steps - alkalization and xanthation (Marani *et al.*, 1980; 1981). Alkalization is achieved by adding starch to alkali solution under constant stirring at room or low temperature. This results in a homogeneous gel. Xanthation is done by adding CS_2 near the bottom of the gel and stirring till the gel turns to homogeneous pale yellow color. This is termed as viscose and is stored at low temperature. The viscose is purified by Amberlite resin (IRA-400 in OH form) to separate low molecular weight sulfur compounds. The concentration of xanthate is estimated through determining degree of substitution (DS) (Swanson *et al.*, 1964; Marani *et al.*, 1980; Rahman, 1971). The typical estimates of DS on freshly prepared xanthates lie in the range of 0.2 to 0.3 (Tare, 1989).

2.6.2 **Metal-SSX Reaction**

Chaudhari (1993) have studied the metal-SSX reactions in details. A summary on the relevant portions of his thesis is reproduced as follows:

- The interaction between metal ions and xanthate is a chemical reaction which is governed by the associated formation constant. The reaction can be represented by (Chaudhari, 1993)



The formation constant K for metal-SSX system can be defined as:

$$K_{m-ssx} = \frac{R(a(X_m M))^{aM-n}}{(RX)^m (M)} \quad (2.6)$$

The solubility product (K_{sp}) for such a specie is postulated (Benefield *et al.*, 1982) to have inverse relationship with the formation constant (K_{m-ssx}).

- The metal-SSX specie is insoluble only when the charge becomes zero. In an aqueous environment with metals having higher K_{sp} values, there would be higher concentration of free metal ion or free xanthates or both compared to metals with lower K_{sp} values. Increasing metal concentration or SSX or both will drive the Equation 2.5 to the right side. But for the first case, particle aggregation will be preferred because of low negative charge, whereas in the second case higher number of free xanthate sites will make particle aggregation difficult due to electrostatic repulsion.
- Metal removal by SSX depends largely on the flocculation of SSX by metallic specie. Efficiency of SSX flocculation depends largely on the critical metal concentration. The critical metal concentration is defined as the lowest initial metal concentration required to form overall neutral metal-SSX specie. In metal-SSX system, since the stoichiometry is attained only at initial metal concentration, equal to or greater than the critical concentration, so critical concentration can be approximated as stoichiometric concentration.

For metals with lower K_{sp} values, the critical metal concentration would be very low and hence such metals are expected to be removed effectively. On the other hand, metals with high K_{sp} values, the stoichiometric metal concentration would be high and hence low levels of residuals metal concentration cannot be achieved, without the application of other flocculating agent.

- It is hypothesized that the specie formed in metal-ethyl xanthate system will be similar to metal-SSX system due to the flexibility of base material (hydrolyzed starch). Wing *et al.* (1974) had given the K_{sp} values of certain metals in metal-ethyl xanthate system. They had shown that an inverse relationship exists between metal removal by SSX and metal-ethyl xanthate K_{sp} values.
- In a metal-SSX system with fixed initial metal concentration but varied SSX doses, the metal removal increases up to certain dose (termed as optimum dose in the literature, Tare, 1989) and exceeding this dose metal removal deteriorates.
- Increase in ionic strength improves metal removal by SSX (Tare and Chaudhari, 1987; Lokesh and Tare, 1989; Tare, 1989).
- In the aqueous environment, SSX can be visualized as negatively charged hydrophilic colloids. When SSX dose exceeds optimum value, metal-SSX dispersions are reported to have considerable net negative charge.

- Reaction of metals with xanthate may be a one-step process, when metal ions are coordinated with xanthate groups or, a two-step process if the metal involved undergoes change in oxidation state. In the previous literature metal-SSX reaction was reported as precipitation reaction. But from the later observations, like increase in metal removal with increase in ionic strength, optimum dose required for effective metal removal, negative charge on metal-SSX specie beyond optimum dose, it can be said undoubtedly, that metal-SSX reaction is a colloid-metal reaction.

Some of the major attractions with starch xanthate process as reported by Wing (1974) are:

- achievements of low residual metal concentrations satisfying the required discharge limit.
- volume of sludge produced is small as compared to alkaline treatment. Metals having K_{sp} values, corresponding to metal-ethyl xanthate, less than 10^{-12} are completely removed.
- the physical nature of sludge is not gelatinous like alkaline treatment and at optimum dose the floc settles well and are easily separable.
- it can be used at a wide range of pH (from 3 to 11).
- estimation of contaminants, introduced in water for removing metal by SSX process, indicated that their levels are quite low.

2.7 Insoluble Starch Xanthate (ISX)

The main difference between ISX and SSX is in the base material. In ISX crosslinked starch is used instead of soluble starch.

Crosslinking of starch leads to increase in particle size of the xanthated product which forms unstable dispersion in aqueous environment.

2.7.1 **Synthesis of ISX**

The synthesis procedure of ISX involves three steps, namely crosslinking, xanthation and washing/drying. The synthesis procedure was first developed by Wing *et al.* (1975); Wing and Rayford (1977); Wing (1978) and Wing (1979). The washing step was modified by Chaudhari (1993). Corn starch (100 g) is slurried in distilled water (150 ml) containing sodium chloride (1.5 g) and epichlorohydrin (5.5 ml). In this slurry potassium hydroxide (6 g) in distilled water (40 ml) is added and the mixture is stirred for 16 hours. This step is termed as crosslinking of starch. The suspension is then treated with NaOH and carbon-di-sulfide added near the bottom. The mixture is stirred for 4 hours. This step is known as xanthation step.

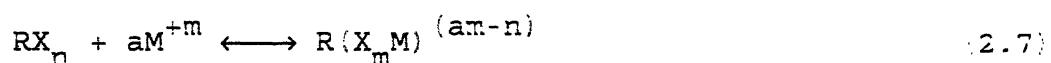
After xanthation distilled water is added in the mixture and allowed to settle for 6 hours and the supernatant is withdrawn. This procedure is repeated four to five times to remove excess alkali and then it is washed with acetone (1500 ml). The prepared xanthate is stored at low temperature in closed bottles. The ISX so prepared is light yellow colored product having 78.12% of starch. The degree of substitution (equivalents of SX groups per glucosidic unit) is ≈ 0.090 (Chaudhari, 1993).

2.7.2 Metal-ISX Interaction

Metal-ISX interaction has been analysed by Chaudhari (1993).

A summary of the relevant portions is presented as follows:

- Metal-ISX interaction is reported to be a sorption process since it involves the transfer of metal ions to the solid phase (ISX), which is easily separable from aqueous system.
- Metal and/or its aqua complexes coordinate with xanthate groups depending upon the affinity and stoichiometry and can be described by the following overall reaction:



The formation constant K_{m-ssx} can be defined as:

$$K_{m-ssx} = \frac{R(X_m^a M)^{(am-n)}}{(RX)^m (M)} \quad (2.8)$$

- The stoichiometry of metal xanthate reaction would depend upon the valency of the metal ions or its aqua complex coordinating with xanthate sites and the mechanism of coordination. In general, monodentate, bidentate and multidentate coordination is possible. The mechanism of metal-ISX coordination may involve coordination of metal ions with xanthate sites or reduction of metal ions followed by coordination with xanthate sites. In general all monovalent metal ions are expected to have monodentate coordination, however some metal ions having high valency may have this coordination, if reduction of metal ion

occurs. With Hg(II) the coordination is monodentate. All divalent metal ions like Cu(II), Cd(II), Ni(II) are expected to make bidentate coordination. Metal ions having valency more than two, make multidentate coordination depending on the valency. For example, trivalent chromium forms tridentate complex.

- The selectivity of metal for xanthates is according to the reciprocal of the K_{sp} values of corresponding metal-ethyl xanthate. Lower the K_{sp} values higher will be the removal.
- Metal-ISX interaction in aqueous phase is governed by metal-xanthate coordination and decomposition of xanthate. The decomposition of ISX is slower than SSX. The rate of decomposition increases with decrease in pH and also with the presence of oxidizing agents. Metal ions have no influence on xanthate decomposition (Wanger et al., 1986).

2.7.3 Relevant Reported Observations on Application of ISX for Heavy Metal Removal

Most of the studies on metal removal using insoluble starch xanthates have been carried out by Wing's group at Peoria, Illinois, USA and Tare's group at Environmental Engineering Laboratory, Indian Institute of Technology, Kanpur, India. The relevant reported observations are summarised as follows:

- ISX removes heavy metal from aqueous phase in single as well as multi-metal systems. Increase in ISX dose resulted in increased metal removal (Wing, 1974).

- In a laboratory study Wing and Rayford (1976) showed efficient removal of eleven different heavy metals by ISX. In most cases the metal concentrations below discharge limits were achieved. ISX's average capacity is reported as 1.1 to 1.5 meq of metals/g ISX. It is effective over pH range 3-11 with maximum effectiveness above pH 7 (Wing and Rayford, 1976). However, in contradiction to this Tare (1989) report that maximum removal efficiency of ISX is achieved at pH 4 to 5.
- Salt concentrations up to 10% have little influence on the effectiveness of ISX (Wing and Rayford, 1976).
- ISX-metal sludge settles rapidly and dewateres to 50 to 90% solids after filtration or centrifugation (Wing and Rayford, 1976).
- Treatment is possible in batch type or continuous flow systems. As reported by Wing and Rayford (1976), if initial concentration of metal ion exceeds 100 mg/l, it may not be economical to use ISX, and removal by precipitation or other processes could be used. In such case, ISX can be used in secondary treatment to further lower metal concentrations below discharge limits.
- Preliminary cost estimate to make ISX is US\$ 0.30/lb (Wing and Rayford, 1976).

2.8

Comparative Evaluation of SSX and ISX

The review of literature presented in previous two sections reveal that both types of xanthates are capable of achieving aqueous phase metal concentrations much below the regulatory effluent standards. Although both types of xanthates are quite effective in metal removal, each has certain merits and demerits over the other. Selection of a particular one is possible only from a detailed comparative study. To make the comparative evaluation realistic, a study (Chaudhari, 1993) was conducted considering:

- synthesis procedure and storage of xanthates,
- efficiency in metal removal,
- cost of chemicals, and
- degree of skill involved in the process.

Comparison of soluble and insoluble starch xanthate process for metal removal is presented in Table 2.2.

2.9

Evaluation of Insoluble Agrobased Xanthate (IAX)

Comparative evaluation of both type of xanthate process reveals that, insoluble xanthates are much more expensive than the soluble one, whereas the former has an edge over the latter in terms of process reliability and operation. It is the elaborate crosslinking step, to make insoluble starch, which make insoluble xanthate expensive. Modifications were originated with exploring low cost, naturally available, insoluble agro-based materials as an alternative to soluble corn starch for xanthation. It was assumed that, these

Table 2.2: Comparative Evaluation of SSX and ISX (Source: Chaudhari, 1993)

Parameter	ISX	SSX
<u>Chemical Requirements:</u>	Per Kg	Per Kg
Corn starch	780 g	210.6 g
NaOH	375 g	50.95 g
CS ₂	102 ml	44.16 ml
NaCl	11.7 g	
Epichlorohydrin	58.6 ml	
KOH	47 g	
Acetone	11.72 l	
Cost of Synthesis	Rs.1430 per Kg	Rs.25 per Kg
Synthesis Time	90 - 110 h	4 - 6 h
Stability on Storage for 6-8 months	Insignificant effect	15-20% reduction in metal removal capacity
Operational Sophistication Required	Less	More
Operational skill Required	Less	More

materials having abundance of hydroxyl group is accessible for xanthation and its' fibrous nature would have improved engineering properties compared to ISX. Different base materials were chosen and their metal removal potential is available from literature (Chaudhari, 1993). The base materials studied include activated carbon, bituminous coal, amberlite resin, coconut shell, sugarcane baggase, corn stalk, and deodar wood.

Out of these seven base materials, the first four were discarded after preliminary study. The first two were proved as

ineffective for removing metal after xanthation. Coconut shell caused problem because of high lignin fraction and resin was discarded because of high costs. The remaining three materials were tested and shown significant metal removal. The products synthesized from these base materials, after xanthation was assumed to be xanthates and are collectively called as insoluble agrobased xanthate (IAX).

2.9.1 Synthesis of IAX

The synthesis procedure for IAX was developed by Chaudhari (1993) on the basis of SSX and ISX synthesis. In 30 g of crushed base material 500 ml sodium hydroxide (160 g/l) was added and stirred for 3 hours. In the mixture 25 ml carbon-di-sulfide was added and stirred for another 4 hours. Then it was allowed to settle for 2 hours and supernatant was decanted. Excess sodium hydroxide was removed by washing with distilled water. Then it was washed by 250 ml acetone. The prepared xanthate was dried and stored in tightly stoppered bottle at low temperature.

2.9.2 Metal-IAX Interaction

The concept of IAX synthesis and application on metal removal was floated and studied by Chaudhari (1993). Through his studies following understanding has been reached:

- IAX particles posses net negative surface charge, which reduces after reacting with metal ions.

- The three types of IAXs (synthesized from wood shavings, baggase and corn stalk) are quite effective in metal removal, both in single and mixed metal systems. Selectivity of metal is according to the reciprocal of the K_{sp} value of the corresponding metal-ethyl xanthate.
- The kinetics of metal-IAX system is slower than the kinetics of metal-ISX system, due to rigid and fibrous nature of the base material.
- In the absence of established technique for xanthate functional groups on the surface of IAXs similarity between IAX and ISX characteristics is established. It is postulated that BX, CSX and WX posses xanthate functional group on the surface since IAX and ISX both are insoluble and exhibit similar behaviour in EPR study, selectivity of metal, and particle charge.

2.10 Recovery of Metal from Metal-Xanthate Sludge

Metal xanthate interaction in aqueous phase is governed by two factors - metal-xanthate coordination and xanthate decomposition. Metal removal from xanthate is possible under aqueous phase condition, where decomposition or removal of free xanthate is rapid or the formation of other soluble species of metals is favoured over metal-xanthate coordination. Very limited studies have been done on metal recovery from insoluble xanthate. As reported by Chaudhari (1993):

- Metal recovery is possible under acidic condition, by mineral acids (sulfuric, hydrochloric and nitric acids) and by oxidizing agents (e.g. hydrogen peroxide, chlorine solution, etc.). Effective metal removal is reported for ISX and IAX both and nitric acid was most effective mineral acid in metal recovery.
- The metal recovery order is just the opposite of metal-xanthate selectivity order, since less driving force is necessary to bring the metal in aqueous phase from solid phase.

2.11 Summary Remarks

The review of literature presented reveal a picture of the development of IAX process, covering IAX synthesis, metal-IAX interaction and metal recovery from metal-IAX sludge. There is little doubt about establishment of xanthate functional groups on the three types of insoluble agro-based materials. Also it has been very well demonstrated that IAX's can be used for effective metal removal in aqueous systems. However, there are several issues, related to insoluble agro-based xanthates synthesis and application, which are not yet fully addressed. Some of these can be stated as follows:

- Role of various parameters such as (i) strength, quantity and type of alkali; (ii) stirring/mixing and contact time during alkalization; (iii) quantity of CS_2 ; and (iv) stirring/mixing and contact time during xanthation in synthesis of IAX.
- Identification of additional base materials for synthesis of IX's.

- Understanding decomposition phenomenon of IAXs and establishing its kinetics.
- Role of various metal releasing/recovery agents for precious metal recovery from IAX's.
- Quick and reliable measure for assessing degree of xanthation in IAX and correlation with metal removal efficiency.

3. OBJECTIVES AND SCOPE

Review of the literature presented in the previous section gives a brief historical development of insoluble agrobased xanthate (IAX) process starting from initially proposed soluble starch xanthate (SSX) process. It has been established beyond doubt that IAXs have high potential in heavy metal removal and can permit recovery of precious metals. As such IAX process appears to be very interesting and promising, particularly for developing countries like India. However, as mentioned in the preceding paragraph, there are several issues which need to be addressed in order to further improve upon the overall effectiveness of the process. The main thrust of the present study is to improve upon the state-of-the-art with an emphasis on either developing more efficient insoluble xanthates or reducing the cost incurred in synthesis or both.

Thus in the present investigation, attention is focused on analysis of the synthesis process of IAXs. Main objective of the study is to investigate the effect of various parameters during synthesis on the potential of IAXs so as to arrive at the appropriate synthesis

conditions. The following two aspects are considered while investigating the synthesis conditions:

1. To obtain IAXs having higher metal removal potential, and
2. to reduce the synthesis cost.

The logical approach to investigate the synthesis condition is to characterize individually all the variables which are involved in xanthation and then analysing their effect. The variables/factors involved in synthesis of xanthates include:

- Base materials selection
- Alkali strength
- BM-Alkali ratio
- Alkalization mixing time
- Alkalization contact time
- Types of alkali
- Reuse of alkali
- Quantity of CS_2
- Xanthation stirring time
- Xanthation contact time.

No established technique is available to measure directly the amount of xanthate groups present on insoluble xanthate. As such the present study is also directed to find out an easy, less skillful and less expensive method to measure the potential of insoluble xanthate over the elaborate and complicated metal-IAX experiment involving residual total metal analysis. The efficiency of insoluble xanthate is related to the density of xanthate functional groups.

4. EXPERIMENTAL METHODOLOGY

In order to achieve the objectives stated in previous section the experimental investigation was carried out in three parts. The first part was mainly aimed at the synthesis of insoluble agrobased xanthates (IAX's). The second part experiments were conducted to analyse the potential of IAXs in metal removal using Cu(II) as model metal. The third part experiments were carried out to observe correlation between iodine consumption and copper loading.

4.1 Part-I Experiments: Synthesis of IAXs

The synthesis of insoluble xanthates involves: (i) use of base materials on which xanthate functional groups can be established, and (ii) adoption of suitable xanthation conditions. In the present study three base materials, namely - sugarcane baggase, corn stalk and wood shavings were chosen. Xanthates prepared from them are collectively called insoluble agrobased xanthates (IAXs) and individually labeled corresponding to the base material used. Xanthates synthesized from baggase, corn stalk and wood shavings have been respectively referred as Baggase Xanthate (BX), Corn Stalk Xanthate (CSX) and Wood Xanthate (WX). The IAX's were synthesized as per the procedure developed by Chaudhari (1993). However, various parameters as reported in Table 4.1 were altered in accordance with the objectives of the study. Only one variable was changed at a time keeping all others fixed. The outline of the synthesis procedure is given as follows:

Table 4.1: Variables Involved in Xanthate Synthesis for a Given Base Material

Steps	Variables	Variations/Range
Alkalization	Chemicals	Sodium hydroxide Potassium hydroxide Lime
	Alkali strength	(1 - 8) M/l
	BM-Alkali ratio	(0.375-1.125)
	Stirring time	(0-3) h
	Total contact time	(1-12) h
Xanthation	CS ₂ -BM ratio	(0-3.8)
	Stirring time	(0-4) h
	Total contact time	(1-12) h

A weighted quantity of the crushed/grinded base material was taken in a 500 ml polyethylene beaker/bottle. To this was added a measured volume of selected alkali of chosen strength. The contents of the beaker/bottle were stirred using mechanical paddle stirrer (Remi Stirrer, 1/8 HP, Remi Udyog Ltd., Bombay) for a set stirring time. After stirring the contents were allowed to stay as it is to permit base material and alkali contact, if contact time was more than stirring time. This step is referred as alkalization. After alkalization, a measured volume of carbon-di-sulfide was introduced at the bottom. Stirring was done as before for a set time. The reaction between CS₂ and alkalized base material was allowed to continue without stirring if the chosen contact time was more than the stirring time. This step is referred as xanthation step. After decanting the mother liquor, the contents of the beaker/bottle were washed with water to remove excess mother liquor. This was followed by washing

with acetone to permit quicker drying. The prepared xanthate was then dried and stored in tightly stoppered polyethylene bottles at low temperature.

4.2 Part-II Experiments: Evaluation of Metal Uptake Capacity of IAX

Metal uptake capacity of xanthate is evaluated by conducting sorption test in a non-flow agitated system using end-over-end shaker as metal-insoluble xanthate interaction involves transfer of metal ions (sorbate) from aqueous phase to solid phase (IAX as sorbent). Cu(II) was chosen as model metal and all tests were done at fixed aqueous environmental conditions. The experimental solution mixture was prepared using 20 ml/l stock copper solution, 125 ml/l acetate buffer (1 M), 12.5 ml/l potassium nitrate solution and 625 ml/l distilled water. The ionic composition of the experimental solution mixture is presented in Table 4.2. Stock copper solution was prepared by dissolving 3.928 g of copper sulfate in triple distilled copper free water, so as to give 1000 mg/l of copper. Acetate buffer was prepared by dissolving 1 M sodium acetate and 1 M acetic acid in proportion as given in Lurie (1975). 80 ml of the experimental solution mixture was transferred to 100 ml polyethylene bottles (37 mm diameter and 100 mm height). The required dosages of IAXs were added and the bottles were fixed on an end-over-end shaker to permit sorbate-sorbent contact for 240 minute. This contact time is considered to be appropriate to achieve equilibrium conditions as reported in literature (Chaudhari, 1993). The supernatant were withdrawn allowing 5 minutes settling time following the equilibrium period and stored in 30 ml polyethylene bottles by adding nitric acid

to lower the pH and subjected to copper analysis using Atomic Absorption Spectrophotometer. A summary of experimental conditions employed for sorption equilibria study is presented in Table 4.3.

Table 4.2 : Estimated Ionic Composition of Experimental Solution Mixture

Cation	Concentration (mM/l)	Anion	Concentration (mM/l)
Cu^{2+}	0.3147	SO_4^{2-}	0.3147
Na^+	79.33	CH_3COO^-	125.0
K^+	0.125	NC_3^-	0.125

Table 4.3 : Summary of Experimental Conditions Employed for Sorption-Equilibria Test

Total Equilibria Time = 240 min
 Temperature = 12 - 15°C

Parameter	Value/Range
Initial copper concentrations	20.0 mg/l
pH	5.0
Ionic strength	0.01
Mixing time	4 h
IAX dose	0.125-0.75 mg/l

4.3 Part-III Experiments: Estimation of Iodine Value

Iodine value for IAX's is determined by estimating the reducing sulfur groups by oxidation-reduction titration using iodine. A mixture of 10% (v/v) 10 ml acetic acid and 10 ml of 0.1 N iodine solution were mixed in distilled water. The mixture was taken in 100 ml polyethylene bottles (37 mm diameter and 100 mm height) and

weighted quantity (2.5 g) of IAXs was added. The bottles were kept on an end-over-end shaker to permit mixing for 240 minutes. After mixing, the solution mixture was titrated with 0.1 N sodium thiosulfate using starch indicator to determine residual iodine. A blank (without IAX) solution mixture of same composition and amount was kept to estimate available iodine. The difference in iodine amount in the blank and with IAX expressed as meq of iodine consumed per g of IAX is referred as iodine value.

4.4 Analytical Techniques

Most of the analytical techniques used were of routine type and were conducted as per the Standard Methods (APHA *et al.*, 1989). A concise statement of the analytical techniques used is presented in Table 4.4.

Table 4.4 : Analytical Techniques Used

Parameter	Instrument/Analytical Techniques	Reference
pH	Digital pH meter, Model No. 335 Systronics, Ahmedabad, India	
Total metal analysis	Atomic Absorption Spectrometer Varian model Spectra AA 20 BQ	APHA <i>et al.</i> , (1989)
Iodine value	Iodometric Titration for equivalent of sulfur group	Russel <i>et al.</i> (1962)

5. RESULTS AND DISCUSSION

In order to study the role of various parameters in the synthesis of IXs for the purpose of heavy metal removal from waters, with the view to either improve their metal uptake capacity or to cut

down the synthesis cost or both, the information available in literature regarding synthesis of xanthates was analysed to identify various parameters which could influence the metal removal capacity and/or significantly alter the synthesis cost. The synthesis of IXs involves four steps. The first step is to select the base material which is insoluble in aqueous environment and to which xanthate functional groups can be attached. The xanthate functional groups can be attached only under highly alkaline conditions and hence the second step involved in the synthesis of IXs is the alkalization of the base material chosen. The third step is the xanthation step in which alkalized base material is allowed to react with carbon-di-sulfide to establish xanthate groups. The fourth step is the washing and drying which enables storage of IXs before use without losing the metal removal capacity significantly as xanthates start decomposing in moist environment. In the present study attempt is made to study the alkalization and xanthation step using the three base materials reported to be promising for IXs synthesis (Chaudhari, 1993). The chosen base material are agricultural based and hence insoluble xanthates synthesized from them are collectively called as insoluble agrobased xanthates (IAXs).

5.1 Alkalization Step

The parameters involved in alkalization step are (i) strength of alkali, (ii) stirring or mixing during base material - alkali reaction, (iii) total reaction or contact time required/provided, (iv) type of alkaline solution used, and (v) ratio of the alkali quantity used for a unit quantity of base material. Effect of all these parameters has been studied by varying each of

these over a wide range and analysing the copper(II) loading capacity along with Iodine value which gives a measure of the reducing sulfur groups associated with the xanthate functional groups.

Figure 5.1 presents the copper loadings and iodine value achieved at different IAX's doses as a function of the alkali (NaOH) strength used during alkalization. The copper loading increased as the alkali strength increased up to 4 M. Beyond this there is no significant increase. The trend is similar with all the three base materials except that xanthation capacity is slightly impaired for baggase at higher alkali strength. The results indicate that for maximum xanthation and hence metal loadings, an alkali strength of 4 M is appropriate. However, from the economic point of view an overall analysis is to be made considering the savings in alkali quantity and the higher dosages required to affect the same degree of metal removal. The results presented in Figure 5.1 will be useful in making such an analysis.

The significance of stirring/mixing during alkalization is shown through the results presented in Figure 5.2. Stirring improves the copper loadings but the increase is insignificant in the synthesis of wood xanthate (WX) compared to baggase xanthate (BX) and corn stalk xanthate (CSX). The significance of stirring during alkalization increases in the order WX<BX<CSX. This is probably due to the texture of the base materials. Wood is obviously less porous and hence the alkali diffusion through the pores is likely to be rate limiting and hence stirring may not help in alkalization.

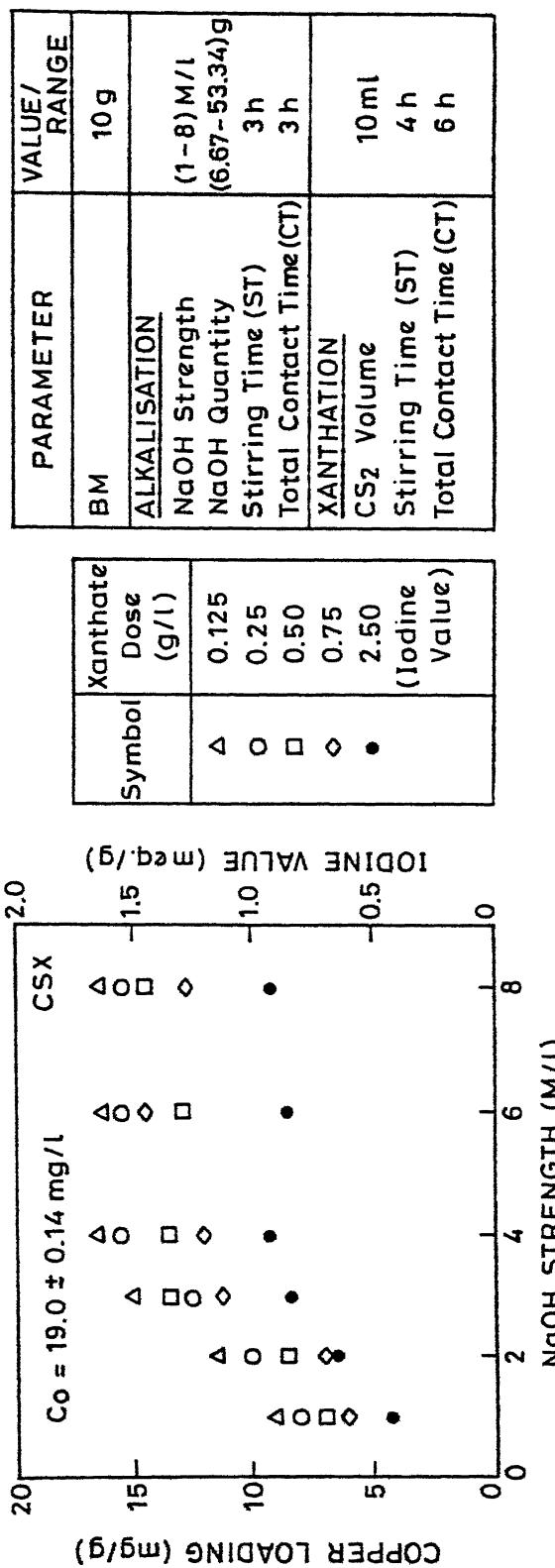
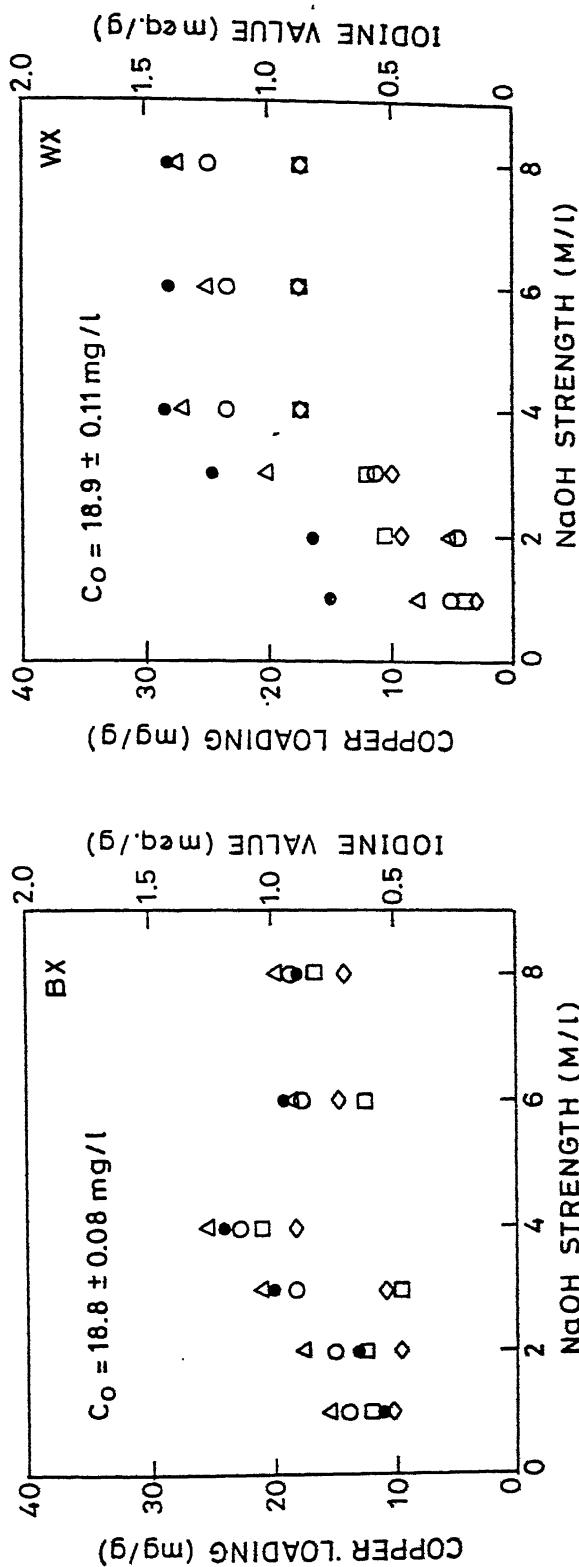


Fig. 5.1 Influence of Alkali Strength on Degree of Xanthation.

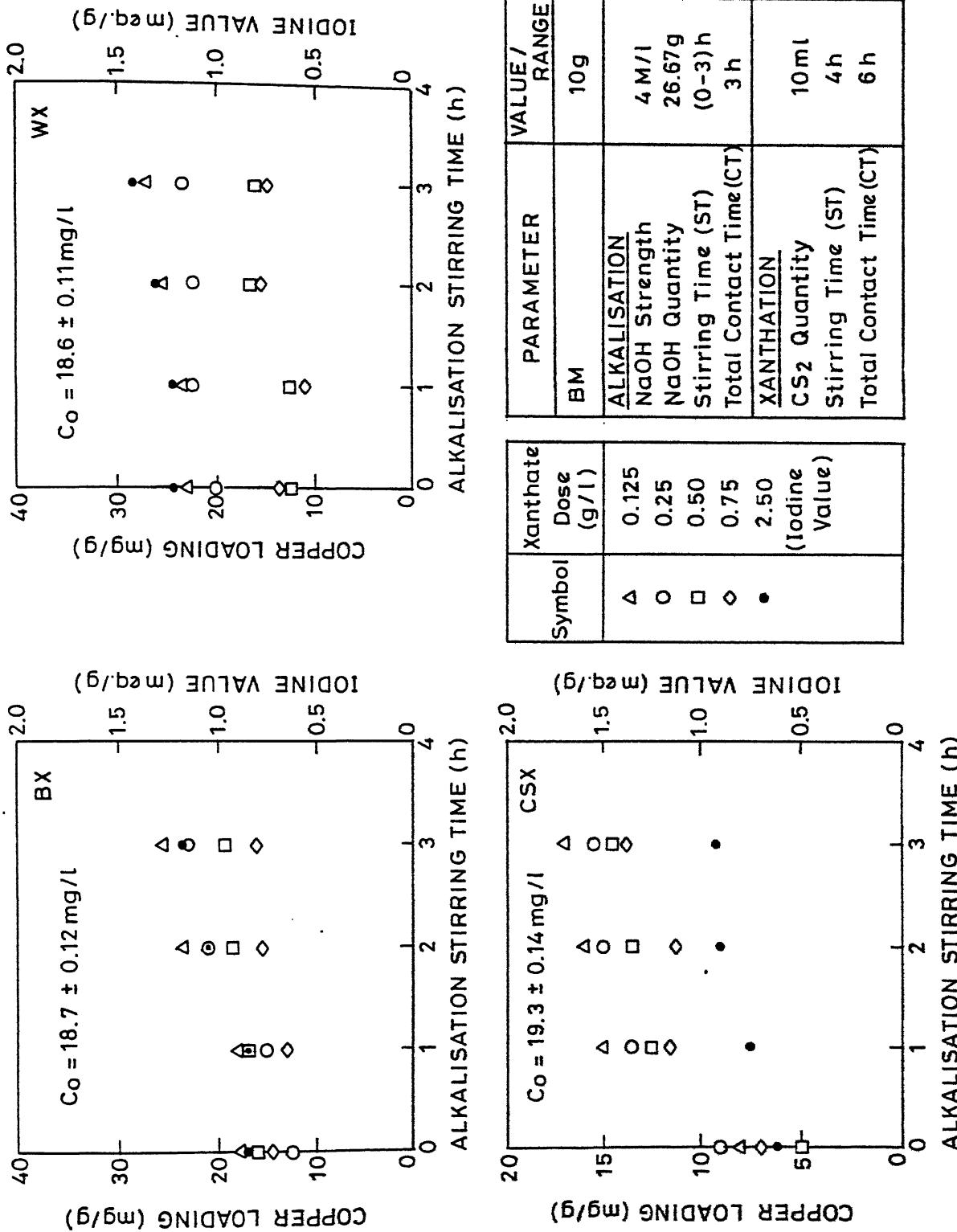


Fig. 5.2 Influence of Alkalisation Stirring Time on Degree of Xanthation.

Figure 5.3 presents the results of experiments done to study the effect of contact/reaction time during alkalization on copper loading capacity for the three types of xanthates. It appears that a contact time of 2-3 h is most appropriate. Increasing the contact times beyond this up to 12 h did not result in any significant increase in degree of xanthation as revealed by copper loadings and iodine values.

The results presented in Figure 5.4 suggest that the quantity of alkaline solution used for a given amount of base material or the amount of base material added to a known volume of alkaline solution insignificantly alters the degree of xanthation for all the three types of xanthates. However, while doing the alkalization step it was observed that the minimum amount of alkaline solution required for a given base material or the maximum amount of base material that can be added to known volume of alkaline solution is governed by ability to completely soak the base material and permit mixing whenever necessary. From this consideration maximum of 180 g of base material could be used per litre of the alkaline solution.

Attempts made to synthesize IAKs using strong (NaOH and KOH) and weak ($\text{Ca}(\text{OH})_2$) bases indicate that both NaOH and KOH give the same degree of xanthation while use of lime results in very low degree of xanthation (Figure 5.5). This may be due to relatively poor solubility of lime resulting in low alkali strength. As reported earlier lower alkali strength results in lower degree of xanthation (Figure 5.1). The reuse of excess alkali by recycling mother liquor leads to almost same degree of xanthation (Figure 5.6) and it appears that the mother liquor could be reused over several cycles as the reduction in alkali

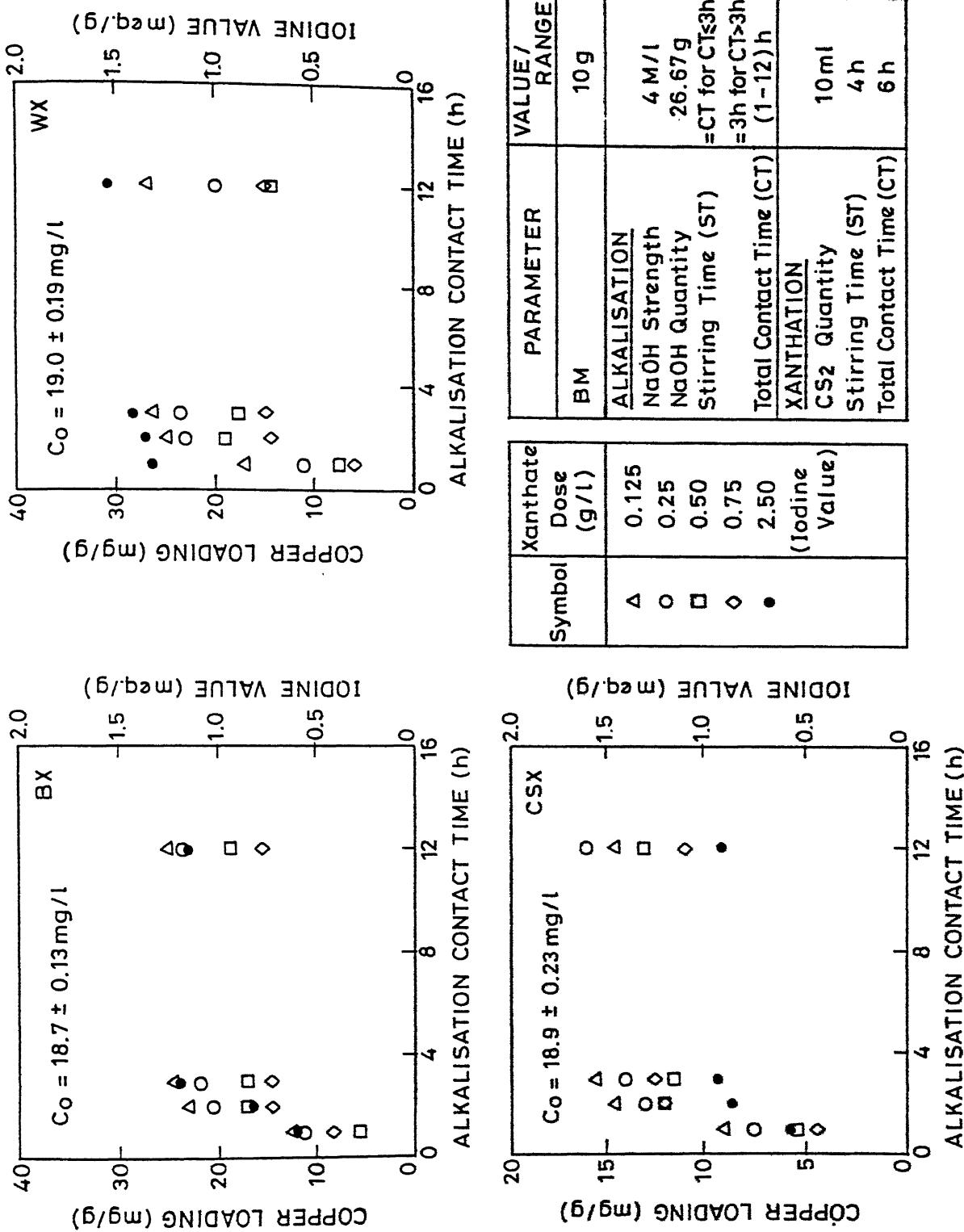


Fig. 5.3 Influence of Alkalisation Total Contact Time on Degree of Xanthation.

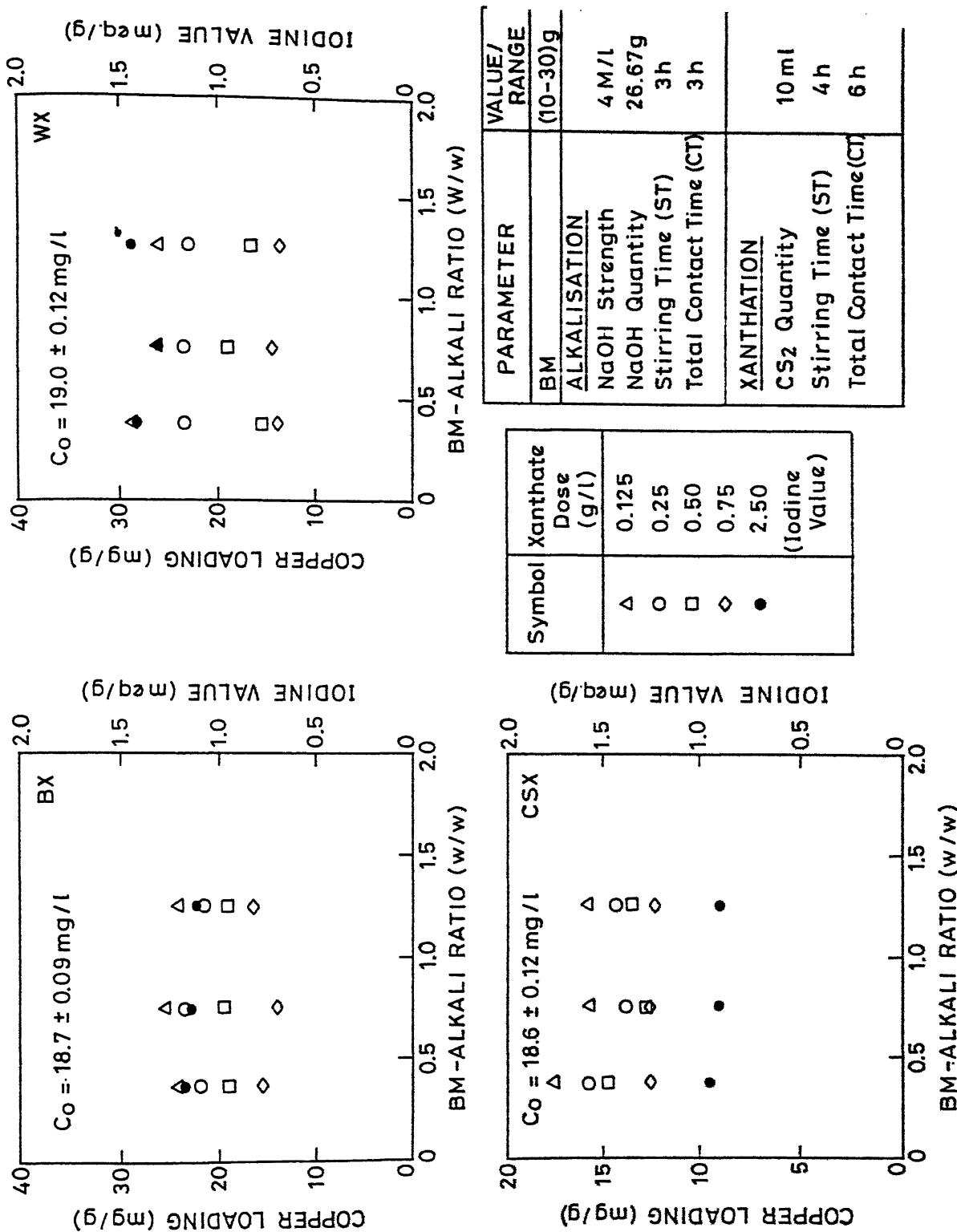


Fig. 5.4 Influence of BM-Alkali Ratio on Degree of Xanthation.

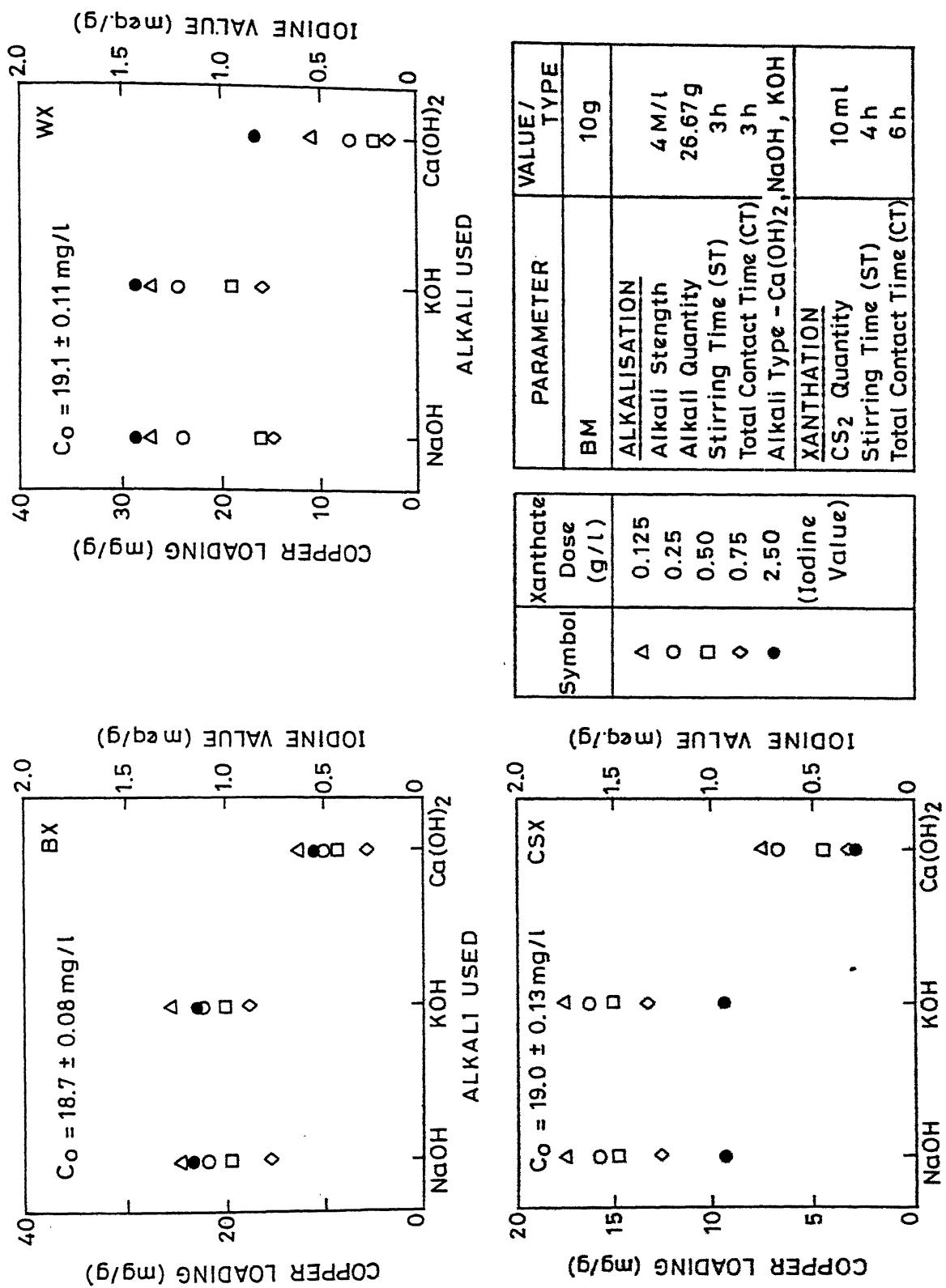


Fig. 5.5 Effect of Different Type of Alkalies on Degree of Xanthation.

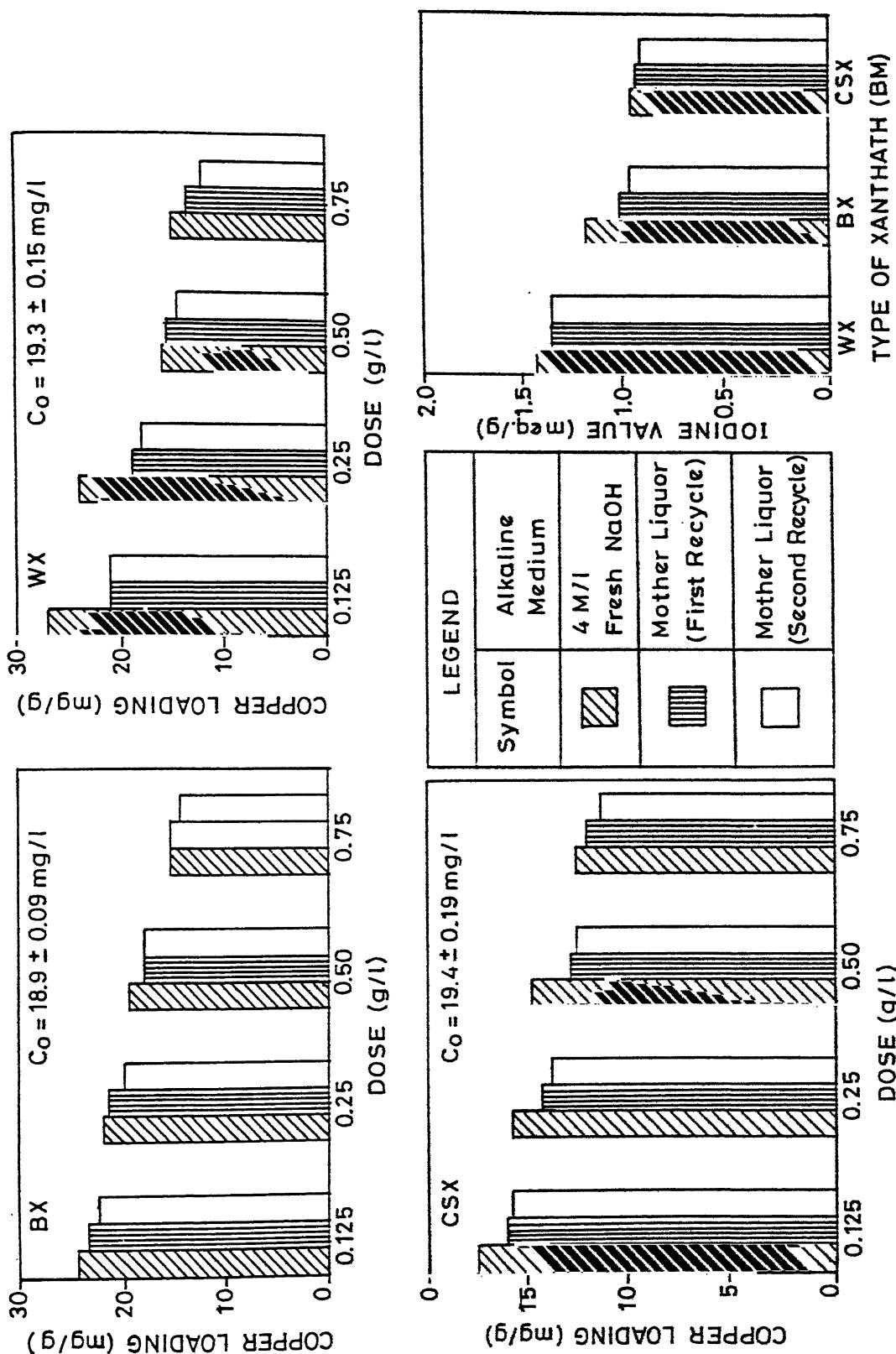


Fig. 5.6 Effect of Reuse of Alkali on Degree of Xanthation.

strength after alkalization or xanthation is negligible. This was confirmed by determining the mother liquor strength by acid-base titration. However, it is suggested that appropriate proportion of base material to alkali volume be used as discussed in the preceding paragraph from the results shown in Figure 5.4 instead of avoidable recycling.

5.2 Xanthation Step

The xanthation step follows the alkalization step and the parameters involved include (i) stirring/mixing during xanthation, (ii) reaction/contact time for xanthation, and (iii) amount of carbon-di-sulfide required/added. As in alkalization step, effect of all these parameters has been studied by varying each of these over a wide range while keeping all other parameters constant and estimating copper(II) loading capacity along with Iodine value.

The results presented in Figures 5.7 and 5.8 reveal that stirring during xanthation step is very important and the degree of xanthation increases with increase in stirring time up to 4 h. Beyond this time additional stirring and contact time do not increase degree of xanthation. Also, the effect of stirring and contact time is similar for all the base materials.

Figure 5.9 presents the results of the experiments done to evaluate the influence of variation in carbon-di-sulfide addition for a unit quantity of base material on degree of xanthation through determining copper loadings and Iodine values. The results indicate that the optimum ratio of carbon-di-sulfide to base material on weight

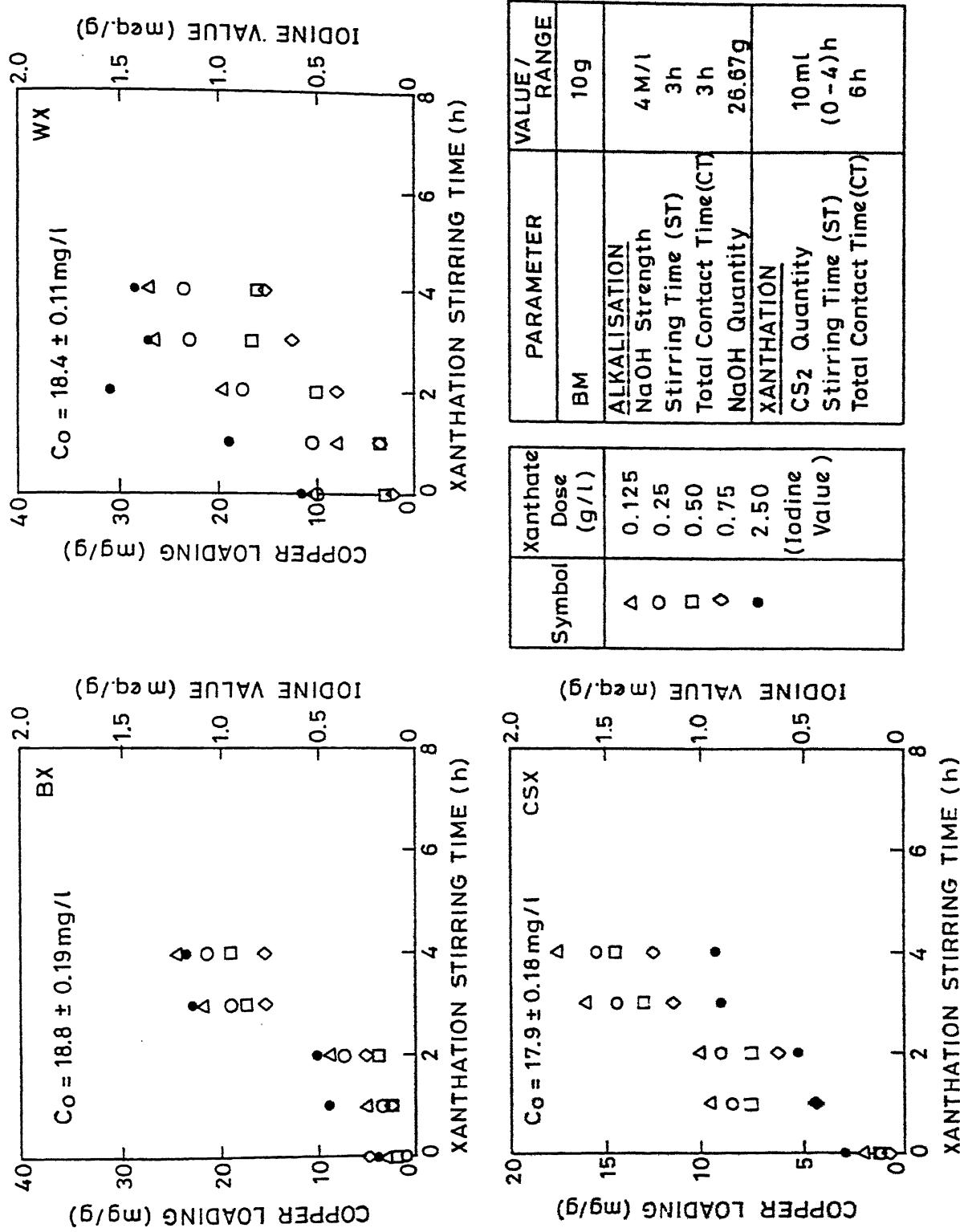
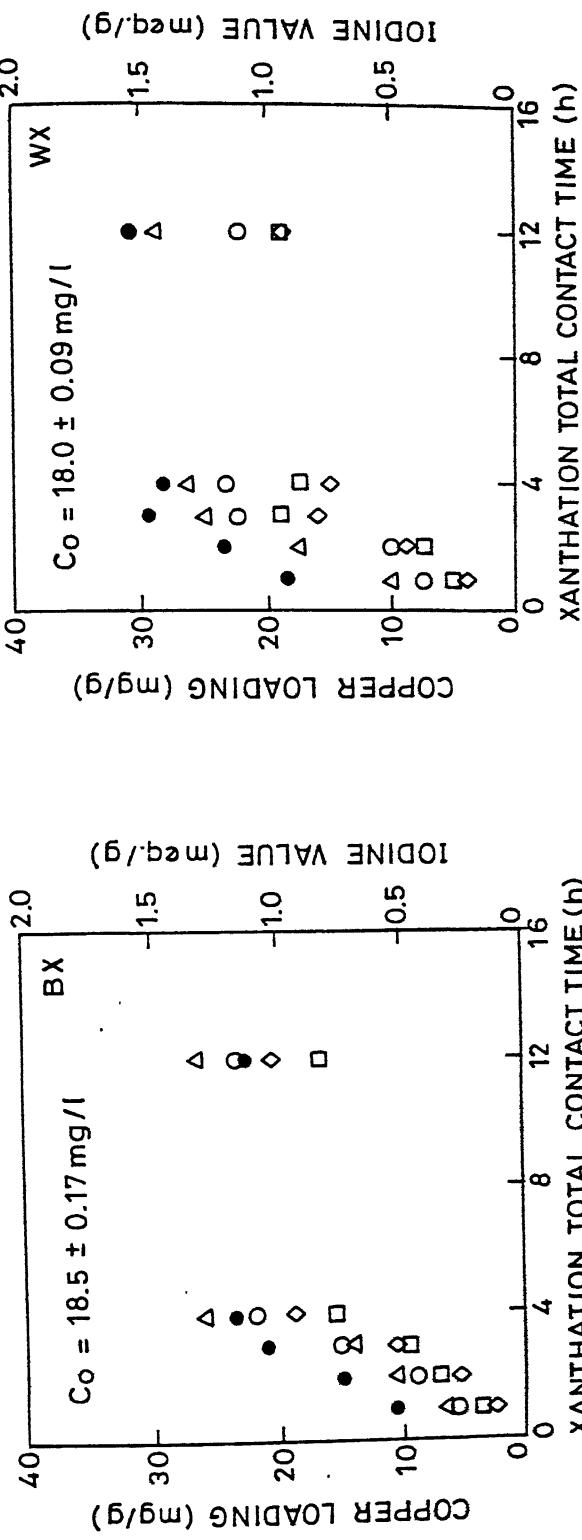


Fig. 5.7 Influence of Xanthation Stirring Time on Degree of Xanthation.



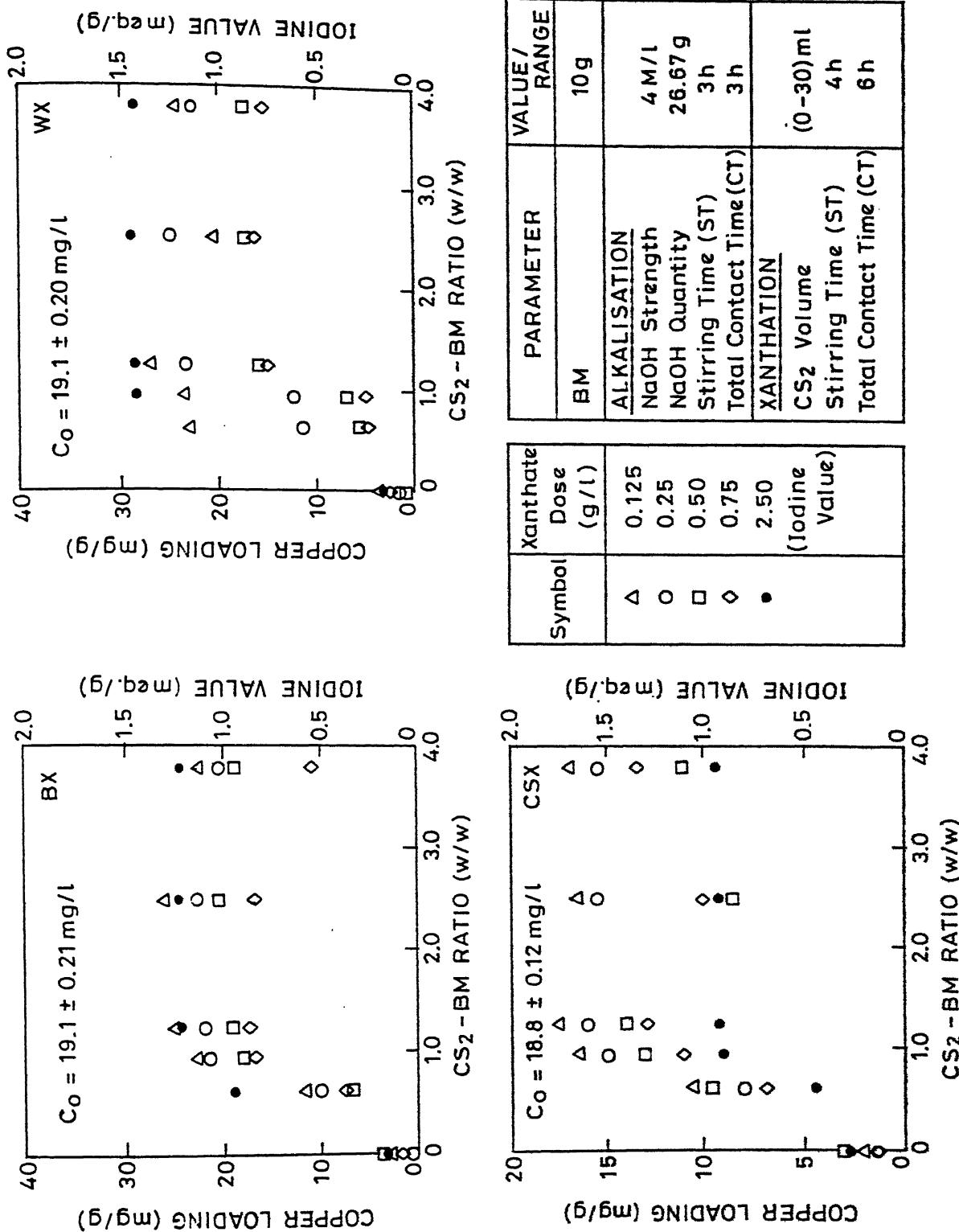


Fig. 5.9 Influence of CS_2 on degree of Xanthation.

basis is around 1.25. The excess addition of carbon-di-sulfide results in lower degree of xanthation as well as lower yield due to solubilisation.

5.3 Correlation between Copper Loadings and Iodine Values

There is no direct and simple test available for quantitative estimation of xanthate functional groups and hence degree of xanthation for IXs. Thus attempt was made to determine reducing sulfur groups of the functional xanthate groups on IXs by equivalent consumption of iodine per unit weight of the xanthate, referred in this thesis as Iodine value, through iodometric titrations. In order to check the effectiveness of iodine value as a measure of xanthate functional groups available for metal binding, correlation between Iodine value and copper loadings is attempted. Results presented in Figure 5.10 indicate that Iodine value and copper loadings are linearly correlated. Hence, it can be said that the Iodine value can as well be taken as an indirect measure of the degree of xanthation and metal binding capacity. The correlation between copper loading and Iodine value and relevant statistical information is presented in Table 5.1.

6. CONCLUSIONS

Based on the results of the present studies and the synthesis of the available information from literature, following conclusions may be drawn:

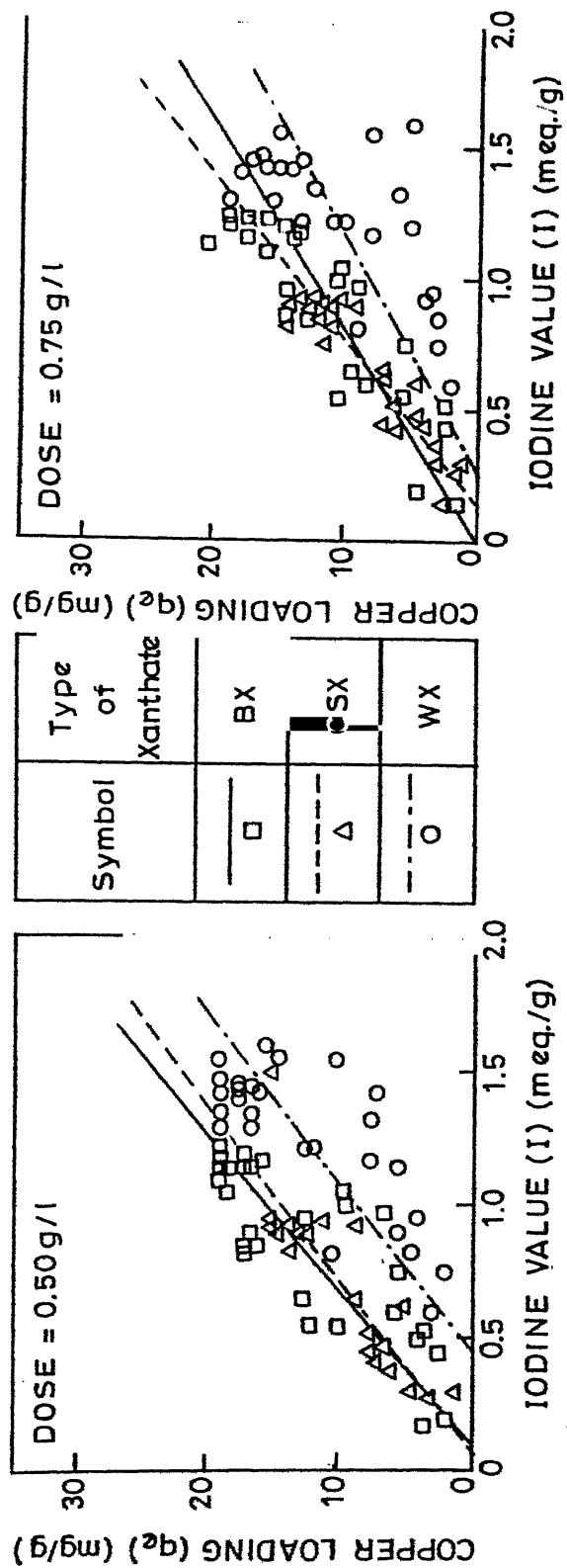
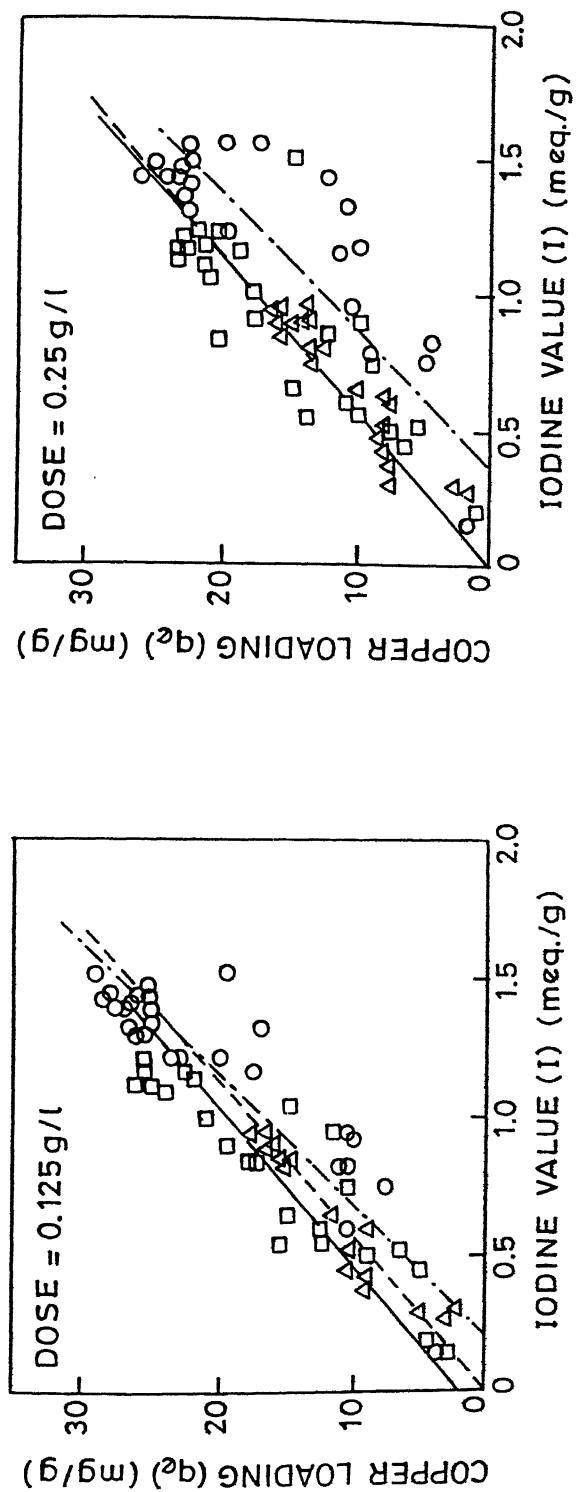


Fig. 5.10 Correlation Between Copper Loading and Iodine Value.

Table 5.1 : Correlation between Iodine Value and Degree of Xanthation with Relevant Statistical Information.

Xanthate dose (g/l)	Type of xanthate	Parameters of Linear Correlation		Coefficient of correlation (R)	Standard error of estimate (S)
		Slope	Intercept		
0.125	BX	17.286	1.925	0.8507	3.8368
	CSX	17.661	0.394	0.9560	1.3827
	WX	20.785	-4.341	0.9038	3.2510
0.25	BX	17.466	0.298	0.8409	3.4297
	CSX	17.328	0.048	0.7273	3.9121
	WX	20.060	-7.618	0.8133	4.4431
0.50	BX	16.911	-1.737	0.8458	3.2965
	CSX	14.952	-0.864	0.9011	1.8167
	WX	15.507	-7.021	0.7492	3.7804
0.75	BX	12.593	0.355	0.8134	3.2249
	CSX	16.288	-2.64	0.9407	1.3893
	WX	11.042	-2.892	0.6878	0.39609

1. For maximum degree of xanthation of IAX's an alkali strength of 4 M appears to be more appropriate. However, from economic point of view optimum alkali strength can be determined by considering reduction in cost due to savings in alkali requirement and increase in cost due to increase in quantity of IAX's required to affect same efficiency of metal removal.
2. The significance of stirring during alkalization increases in the order WX<BX<CSX and is probably related to the texture of the base material.
3. A contact time of 2-3 h is most appropriate during alkalization for synthesis of IAXs for metal removal from waters.
4. The amount of base material that can be added to a known volume of alkaline solution is governed by the ability to completely

soak the base material and permit stirring whenever necessary. For the three base materials, namely wood, baggase and corn stalk, maximum of 180 g of base material could be used per litre of the alkaline solution.

Only strong bases are effective in achieving reasonable degree of xanthation on IAXs.

The reuse of excess alkali by recycling mother liquor leads to same degree of xanthation as fresh alkaline solution.

Stirring during xanthation step is very important and a stirring time of 4 h is required to achieve maximum possible xanthation and is independent of the base materials used.

The optimum ratio of CS_2 :BM is 1.25 for maximum degree of xanthation for all the three base materials used.

A good correlation exists between Iodine value and copper loading and hence Iodine value can be used as a simple measure to get an idea about degree of xanthation and metal binding capacity.

7. SUGGESTIONS FOR FUTURE WORK

On the basis of the experience gained while conducting the present research and identified gaps in information on insoluble xanthate process for heavy metal removal and recovery from waters following suggestions are offered for logical continuation of the present work.

In this thesis information is presented on the influence of various parameters involved in the synthesis of IAXs during alkalization and xanthation on the degree of xanthation for metal removal from waters. This information needs to be integrated with cost analysis so as to work out optimum conditions for synthesis of IAXs.

Efforts should be made to evaluate washing and drying of IAXs and to propose a proper procedure for the same as well as storage.

Additional agrobased base materials which have better engineering properties and higher potential for xanthation should be identified.

Role of various metal releasing/recovery agents for precious metal recovery from metal bound to IAX's needs to be studied in detail. Understanding decomposition phenomenon of IAXs and establishing its kinetics as an initial step in this direction will be useful.

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